CHAPTER NINE

COVALENT BONDING: ORBITALS

For Review

1. The valence orbitals of the nonmetals are the s and p orbitals. The lobes of the p orbitals are 90° and 180° apart from each other. If the p orbitals were used to form bonds, then all bonds should be 90° or 180°. This is not the case. In order to explain the observed geometry (bond angles) that molecules exhibit, we need to make up (hybridize) orbitals that point to where the bonded atoms and lone pairs are located. We know the geometry; we hybridize orbitals to explain the geometry.

Sigma bonds have shared electrons in the area centered on a line joining the atoms. The orbitals that overlap to form the sigma bonds must overlap head to head or end to end. The hybrid orbitals about a central atom always are directed at the bonded atoms. Hybrid orbitals will always overlap head to head to form sigma bonds.

2. geometry hybridization unhybridized p atomic orbitals

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<table>
<thead>
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<tbody>
<tr>
<td>linear</td>
<td>sp</td>
<td>2</td>
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<tr>
<td>trigonal planar</td>
<td>sp²</td>
<td>1</td>
</tr>
<tr>
<td>tetrahedral</td>
<td>sp³</td>
<td>0</td>
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The unhybridized p atomic orbitals are used to form π bonds. Two unhybridized p atomic orbitals each from a different atom overlap side to side, resulting in a shared electron pair occupying the space above and below the line joining the atoms (the internuclear axis).

3. \( \text{H}_2\text{S}, 2(1) + 6 = 8 \text{e}^- \) \hspace{1cm} \( \text{CH}_4, 4 + 4(1) = 8 \text{e}^- \)

\[
\text{H}_2\text{S} \quad \begin{array}{c}
\text{H} \\
\text{S} \\
\text{H}
\end{array}
\quad \begin{array}{c}
\text{H} \\
\text{C} \\
\text{H}
\end{array}
\quad \text{HCN}, 1 + 4 + 5 = 10 \text{e}^-
\]

\[
\text{H}_2\text{CO} \quad 2(1) + 4 + 6 = 12 \text{e}^- 
\]

\[
\text{HCN}, 1 + 4 + 5 = 10 \text{e}^-
\]

\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{H}
\end{array}
\quad \begin{array}{c}
\text{H} \\
\text{C} \\
\text{N}
\end{array}
\]

\( \text{H}_2\text{S} \) and \( \text{CH}_4 \) both have four effective pairs of electrons about the central atom. Both central atoms will be sp³ hybridized. For \( \text{H}_2\text{S} \), two of the sp³ hybrid orbitals are occupied by lone pairs. The other two sp³ hybrid orbitals overlap with 1s orbitals from hydrogen to form the 2

\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{H}
\end{array}
\quad \begin{array}{c}
\text{H} \\
\text{C} \\
\text{N}
\end{array}
\]
S–H sigma bonds. For CH₄, the four C–H bonds are formed by overlap of the sp³ hybrid orbitals from carbon with 1s orbitals on H.

H₂CO has a trigonal planar geometry, so carbon is sp² hybridized. Two of the sp² hybrid orbitals overlap with hydrogen 1s orbitals to form the two C–H sigma bonds. The third sp² hybrid orbital is used to form the sigma bond in the double bond by overlapping head to head with an sp² hybrid orbital from oxygen. The second bond in the double bond is a π bond. The unhybridized p atomic orbital on carbon will overlap with a parallel p atomic orbital on O to form the π bond.

HCN has a linear geometry, so carbon is sp hybridized. HCN has one C–H sigma bond, one C–N sigma bond and two C–N π bonds. The C–H sigma bond is formed from sp–1s orbital overlap. The C–N sigma bond is formed from an sp hybrid orbital on carbon overlapping with an sp² hybrid orbital from nitrogen. The π bonds are formed from the two unhybridized p atomic orbitals from carbon overlapping with two unhybridized p atomic orbitals from N. Each π bond is formed from the p orbitals overlapping side to side. Because the p orbitals used must be perpendicular to each other, the π bonds must be in two different planes that are perpendicular to each other and perpendicular to the internuclear axis.

4. Molecules having trigonal bipyramid geometry have five pairs of electrons around the central atom. We need five hybrid orbitals to account for the location of these five sets of electrons. We use the valence s and the three degenerate p valence atomic orbitals for four of the five orbitals; the fifth is an empty d orbital close in energy to the valence atomic orbitals. We call this hybridization dsp³. For octahedral geometry, we need six hybrid orbitals to account for the locations of six pairs of electrons about the central atom. We use the s and three p valence atomic orbitals along with two empty d orbitals. We mix these six atomic orbitals together and come up with six hybrid orbitals which point to the vertices of an octahedron.

PF₅ and SF₄ both have five pairs of electrons about the central atoms so both exhibit dsp³ hybridization to account for the trigonal bipyramid arrangement of electron pairs. In PF₅, the five pairs of electrons are bonding electrons in the five P–F sigma bonds. Overlap of the dsp³ hybrid orbitals from phosphorus with the appropriate orbitals on each F atom go to form the sigma bonds. SF₄ has four S–F bonds and a lone pair of electrons about the sulfur. Four of the sulfur dsp³ hybrid orbitals overlap with appropriate orbitals on the fluorines to form the four S–F sigma bonds, the fifth dsp³ hybrid orbital holds the lone pair of electrons on the sulfur.

SF₆ and IF₅ both have six pairs of electrons about the central atoms so both exhibit d²sp³ hybridization to account for the octahedral geometries of electron pairs. In SF₆, the six d²sp³ hybrid orbitals overlap with appropriate orbitals from F to form the six S–F sigma bonds. In IF₅, five of the six d²sp³ hybrid orbitals go to form the five I–F sigma bonds with the sixth d²sp³ holding the lone pair of electrons on iodine.

5. The electrons in sigma bonding molecular orbitals are attracted to two nuclei, which is a lower, more stable energy arrangement for the electrons than in separate atoms. In sigma antibonding molecular orbitals, the electrons are mainly outside the space between the nuclei, which is a higher, less stable energy arrangement than in the separated atoms.
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6. See Fig. 9.32 for the 2s $\sigma$ bonding and $\sigma$ antibonding molecular orbitals and see Fig. 9.34 for the 2p $\sigma$ bonding, $\sigma$ antibonding, $\pi$ bonding, and $\pi$ antibonding molecular orbitals.

7. Bond energy is directly proportional to bond order. Bond length is inversely proportional to bond order. Bond energy and bond length can be measured; bond order is calculated from the molecular orbital energy diagram (bond order is the difference between the number of bonding electrons and the number of antibonding electrons divided by two).

Paramagnetic: a kind of induced magnetism, associated with unpaired electrons, that causes a substance to be attracted into an inducing magnetic field. Diamagnetic: a type of induced magnetism, associated with paired electrons, that causes a substance to be repelled from the inducing magnetic field. The key is that paramagnetic substances have unpaired electrons in the molecular orbital diagram while diamagnetic substances have only paired electrons in the MO diagram.

To determine the type of magnetism, measure the mass of a substance in the presence and absence of a magnetic field. A substance with unpaired electrons will be attracted by the magnetic field, giving an apparent increase in mass in the presence of the field. A greater number of unpaired electrons will give a greater attraction and a greater observed mass increase. A diamagnetic species will not be attracted by a magnetic field and will not show a mass increase (a slight mass decrease is observed for diamagnetic species).

8. a. $\text{H}_2$ has two valence electrons to put in the MO diagram for $\text{H}_2$ while $\text{He}_2$ has 4 valence electrons.

\[
\text{H}_2: (\sigma_{1s})^2 \\
\text{He}_2: (\sigma_{1s})^2(\sigma_{1s}^*)^2
\]

Bond order $= \text{B.O.} = (2!0)/2 = 1$

$\text{He}_2$: $\text{B.O.} = (2!2)/2 = 0$

$\text{H}_2$ has a nonzero bond order so MO theory predicts it will exist. The $\text{H}_2$ molecule is stable with respect to the two free H atoms. $\text{He}_2$ has a bond order of zero so it should not form. The $\text{He}_2$ molecule is not more stable than the two free He atoms.

b. See Fig. 9.39 for the MO energy-level diagrams of $\text{B}_2$, $\text{C}_2$, $\text{N}_2$, $\text{O}_2$, and $\text{F}_2$. $\text{B}_2$ and $\text{O}_2$ have unpaired electrons in their electron configuration so they are predicted to be paramagnetic. $\text{C}_2$, $\text{N}_2$ and $\text{F}_2$ have no unpaired electrons in the MO diagrams; they are all diamagnetic.

c. From the MO energy diagram in Fig. 9.39, $\text{N}_2$ maximizes the number of electrons in the lower energy bonding orbitals and has no electrons in the antibonding 2p molecular orbitals. $\text{N}_2$ has the highest possible bond order of three so it should be a very strong (stable) bond.

d. $\text{NO}^+$ has $5 + 6 - 1 = 10$ valence electrons to place in the MO diagram and $\text{NO}^-$ has $5 + 6 + 1 = 12$ valence electrons. The MO diagram for these two ions is assumed to be the same as that used for $\text{N}_2$.

\[
\text{NO}^+: (\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^3(\sigma_{2p})^2 \\
\text{NO}^-: (\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\pi_{2p}^*)^2 \\
\text{B.O.} = (8!2)/2 = 3 \\
\text{B.O.} = (8!4)/2 = 2
\]

$\text{NO}^+$ has a larger bond order than $\text{NO}^-$, so $\text{NO}^+$ should be more stable than $\text{NO}^-$. 
9. In HF, it is assumed that the hydrogen 1s atomic orbital overlaps with a fluorine 2p orbital to form the bonding molecular orbital. The specific 2p orbital used in forming the bonding MO is the p orbital on the internuclear axis. This p orbital will overlap head to head with the hydrogen 1s orbital forming a sigma bonding and a sigma antibonding MO. In the MO diagram, the unpaired H 1s electron and the unpaired fluorine 2p electron fill the $\sigma$ bonding MO. No electrons are in the antibonding orbital. Therefore, HF has a bond order of $(2/0)/2 = 1$ and it should (and does) form.

We also use the MO diagram to explain the polarity of the H!F bond. The fluorine 2p orbitals are assumed lower in energy than the hydrogen 1s orbital because F is more electro-negative. Because the $\sigma$ bonding MO is closer in energy to the fluorine 2p atomic orbitals, we say the bonding orbital has more fluorine 2p character than hydrogen 1s character. With more fluorine 2p character, the electrons in the bonding orbital will have a greater probability of being closer to F. This leads to a partial negative charge on F and a partial positive charge on H.

10. Molecules that exhibit resonance have delocalized $\pi$ bonding. This is a fancy way of saying that the $\pi$ electrons are not permanently stationed between two specific atoms, but instead can roam about over the surface of a molecule. We use the concept of delocalized $\pi$ electrons to explain why molecules that exhibit resonance have equal bonds in terms of strength. Because the $\pi$ electrons can roam about over the entire surface of the molecule, the $\pi$ electrons are shared by all of the atoms in the molecule giving rise to equal bond strengths.

The classic example of delocalized $\pi$ electrons is benzene, C$_6$H$_6$. Fig. 9.47 and 9.48 show the $\pi$ molecular orbital system for benzene. Each carbon in benzene is sp$^2$ hybridized, leaving one unhybridized p atomic orbital. All six of the carbon atoms in benzene have an unhybridized p orbital pointing above and below the planar surface of the molecule. Instead of just two unhybridized p orbitals overlapping, we say all six of the unhybridized p orbitals overlap resulting in delocalized $\pi$ electrons roaming about above and below the entire surface of the benzene molecule.

$$\text{O}_3, \ 6 + 2(6) = 18 \ \text{e}^-$$

Ozone has a delocalized $\pi$ system. Here the central atom is sp$^2$ hybridized. The unhybridized p atomic orbital on the central oxygen will overlap with parallel p orbitals on each adjacent O atom. All three of these p orbitals overlap together resulting in the $\pi$ electrons moving about above and below the surface of the O$_3$ molecule. With the delocalized $\pi$ electrons, the O-O bond lengths in O$_3$ are equal (and not different as each individual Lewis structure indicates).